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WO 94/08235 A WO 90/12315 A

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(54) **Method for identifying causes of faults in amperometric measuring cells**

(57) The method identifies causes of faults in an amperometric measuring cell 1 which has at least an measuring electrode 2 and a counterelectrode 3 in an chamber 4 filled with a soluble electrolyte 6, and separated from the measurement sample being investigated by a permeable membrane 7, and a voltage source 10 of potential U, which produces a reference current i(t) between the electrodes 2, 3. The potential U is raised or lowered to a first potential U_1 during a first period of time T_1, and the resulting first sensor current i_1 is measured and compared with the reference current. The first sensor current may be measured shortly after the adjustment to the first potential U_1, or towards the end of the first period of time T_1. During a second period, following the first period T_1, the potential may be adjusted to a second potential which is less than U if U_1 was greater than U, or greater than U if U_1 was less than U.

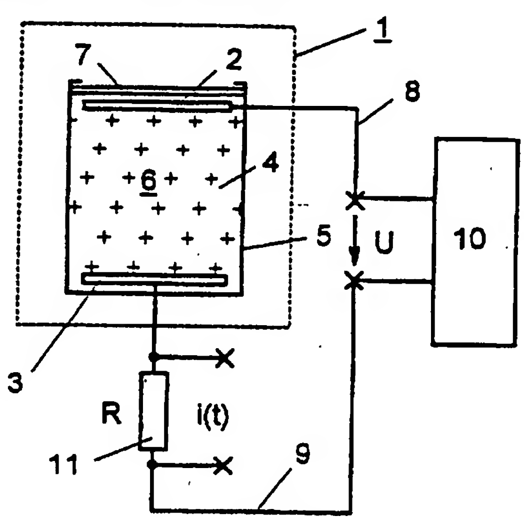

Fig.1

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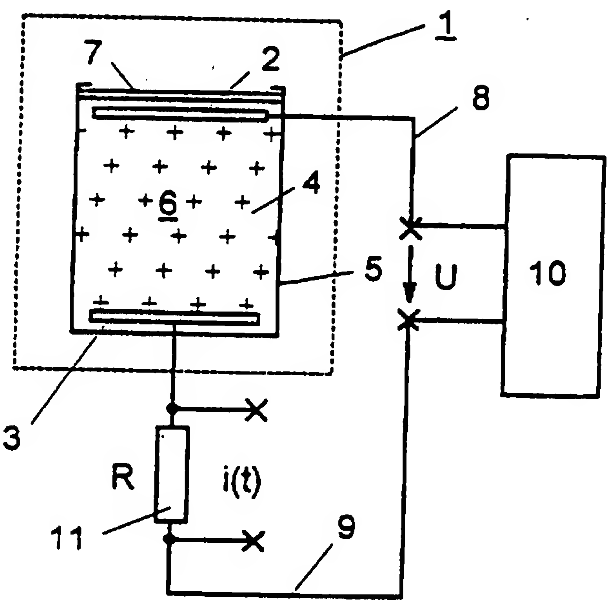

Fig.1

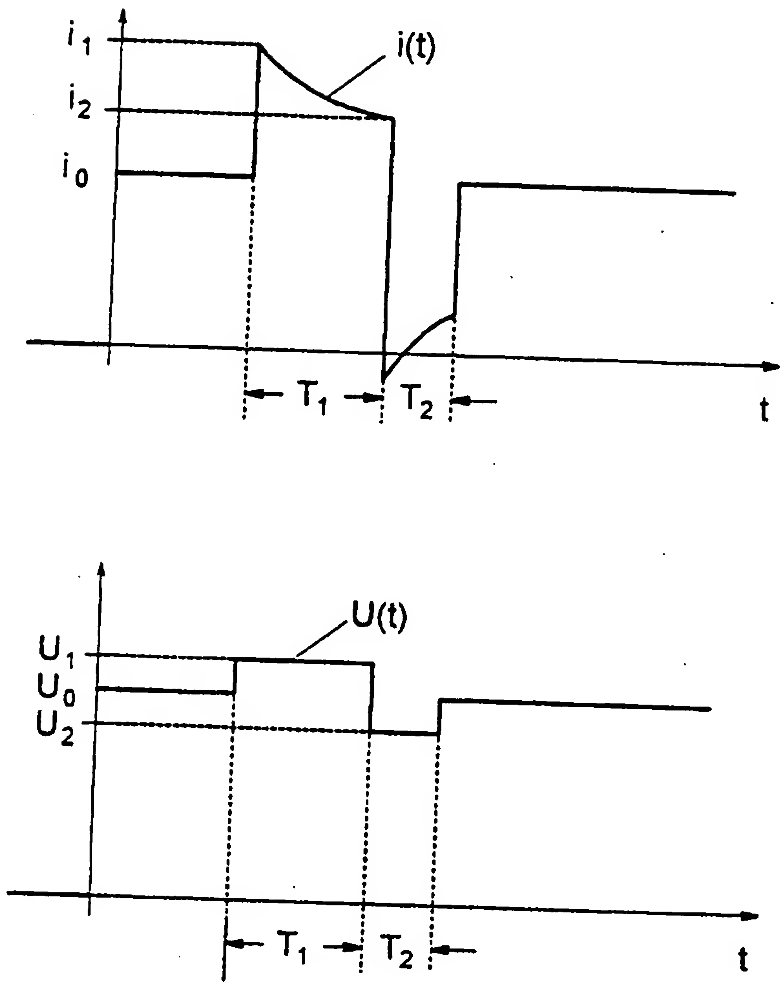

Fig. 2

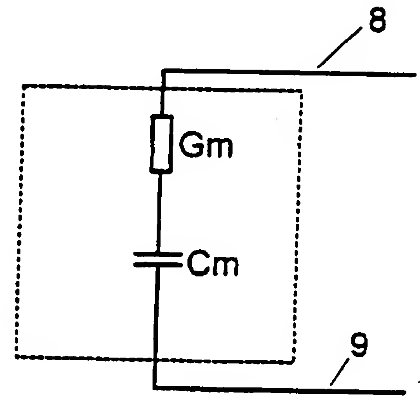

Fig. 3

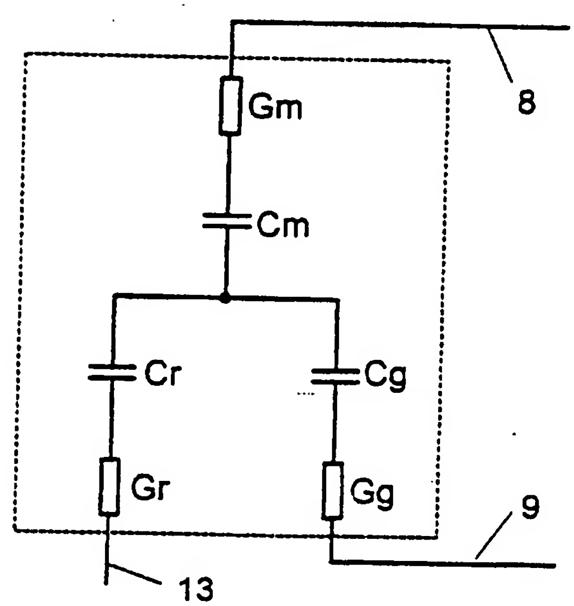

Fig. 4

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METHOD FOR IDENTIFYING CAUSES OF FAULTS IN AMPEROMETRIC MEASURING CELLS

The invention relates to a method for identifying causes of faults in an amperometric measuring cell which has at least a measuring electrode and a counterelectrode in an electrolyte-filled electrolyte chamber, separated from the measuring sample being investigated by a permeable membrane, and which is connected to a voltage source which produces a sensor current between the electrodes and provides a potential.

An electrochemical measuring cell of this kind has been disclosed in DE 38 41 622 C1. A measuring electrode, a reference electrode and a counterelectrode are fitted in an electrolyte-filled electrolyte chamber of a measuring cell housing which is separated from the sample being investigated by means of a permeable membrane. The measuring electrode, the reference electrode and the counterelectrode have measuring connections which are led out through the housing of the measuring cell and are connected to an evaluation unit having a voltage source. After connection of the electrodes to the voltage source a sensor current i(t) begins to flow.

It is a disadvantage of the known measuring cell that it is not possible to obtain any indication of the service condition of the measuring cell. Thus it may, for example, happen that although the sensor current i(t) falls within its predetermined limits, an accurate measurement of concentration is nevertheless no longer possible with the measuring cell.

From EP 419 769 A2 a method for continuous monitoring of an electrode system of potentiometric measuring cells is known in which symmetrical bipolar current pulses of different periods are repeatedly applied to the measuring cell and the change in

potential thereby produced, relative to the electrode potential without current pulses, is compared with a calculated or experimentally determined intended value.

This known process has the disadvantage that an additional voltage source is required by means of which the test is carried out, and that for the detection of the individual faults the test must be performed at different times and using different periods.

The present invention seeks to provide a process for the identification of the causes of faults for amperometric measuring cells by means of which different faults can be identified within one measuring cycle.

According to the present invention, there is provided a method for identifying causes of faults in an amperometric measuring cell which has at least one measuring electrode and a counterelectrode in a soluble electrolyte-filled electrolyte chamber separated from the measuring sample being investigated by a permeable membrane, and which is connected to a voltage source which produces a sensor current between the electrodes and provides a potential, the method comprising the steps of:

applying a reference potential and measuring a reference current flowing due to the application of the reference potential;

applying a first potential, different from the reference potential, during a first period of time and measuring a first sensor current flowing due to the application of the first potential; and

comparing the first sensor current with the reference current.

Thus, starting from a reference potential U_0, with a reference current i_0, a first potential U_1 is applied during a first period of time T_1 and a first sensor current i_1 is measured shortly after the application of

the first potential U_1, and/or a second sensor current i_2 is measured near the end of the first period of time T_1, and the sensor current i_1 and/or i_2 is compared with the reference current i_0.

The advantage of the invention is essentially that through a slight modification of the potential, i.e. by raising or lowering the potential to a first potential U_1 during a first period of time T_1, a change in the sensor current i(t) from i_1 to i_2 is produced, and that the comparison of the first sensor current i_1 and/or of the second sensor current i_2 with the reference current i_0 is used to detect a fault in the measuring cell. To perform this measurement only a slight modification of the potential, in the region of about 0.02 to 1 millivolt, is required. The first period of time T_1 amounts to about 100 milliseconds. If the method of the invention is carried out during the exposure of the measuring cell to the sample of gas to be investigated, the reference current i_0 is the measuring current, and in a neutral gas atmosphere the stationary sensor base current forms the reference current.

The sub-claims are directed to advantageous embodiments of the invention.

Advantageously, during a period of time T_2 following the first period of time T_1 the potential is adjusted to a second potential U_2 which, relative to the reference potential U_0, is directed oppositely to the first potential U_1. This results in reversal of polarity within the measuring cell, and after the end of the second period of time T_2 the reference current i_0 again flows in the measuring cell.

The length of the second period of time T_2 is advantageously not more than 1.5 times the first period of time T_1.

The second period of time T_2 is advantageously calculated by the formula

$$T_2 = T_1 \times \ln(1 - Y \times (1/X))/\ln(X)$$

where

$$X = (i_1 - i_0)/(i_2 - i_0) \quad \text{and}$$

$$Y = (U_1 - U_0)/(U_2 - U_0).$$

Advantageously the parameters C_m and G_m characterising the measuring cells are calculated by the formulae:

$$G_m = (i_1 - i_0)/(U_1 - U_0)$$

$$C_m = T_1 \times G_m/\ln((i_1 - i0)/(i_2 - i_0).$$

The parameters C_m and G_m may, for example, be compared with predetermined values C_{m0} and G_{m0}, an indication being given, if a previously established limiting value is exceeded, that the measuring cell is exhausted or damaged and must be exchanged for a new one.

For a better understanding of the present invention, and to show how it may be brought into effect, reference will now be made, by way of example, to the accompanying drawings, in which:

Fig. 1 shows schematically the design of an amperometric measuring cell with two electrodes,

Fig. 2 shows how the sensor current varies with time on application of the potentials U_1 and U_2,

Fig. 3 is an equivalent circuit diagram of the measuring cell of Fig. 1, and

Fig. 4 is an equivalent circuit diagram of a measuring cell with an additional reference electrode.

Figure 1 shows schematically the design of an electrochemical measuring cell (1) having a measuring electrode (2) and a counterelectrode (3) which are fixed in an electrolyte chamber (4) of a measuring cell housing (5). The measuring cell housing (5) is filled with an electrolyte (6) in aqueous solution and is

separated from the gas sample to be investigated by a permeable membrane (7). The electrodes (2, 3) are connected by leads (8, 9) to a voltage source (10) by means of which a potential U is applied to the electrodes (2, 3). The sensor current i(t) is detected as a potential drop across a measuring resistance (11) in the lead (9).

Figure 2 shows the variation of the sensor current i(t) with time in dependence on the potential U(t). During a first period of time T_1 the potential U is raised to the first potential U_1, so that the sensor current i(t) increases from the reference current i_0 to the first sensor current i_1 and then falls during the first period of time T_1 to the second sensor current i_1. During a second period of time T2 following the first period of time T_1 the potential is lowered to the second potential U_2, and the sensor current i(t) falls relative to the reference current i_0, and after the second period of time T_2 again assumes the reference current value i_0. The sensor currents i_0, i_1 and i_2 are read into an evaluation unit (not shown in Figure 1) which includes a microprocessor that compares the sensor currents and performs calculations. Through the evaluation unit the variations of the potential from U_0 to U_1 and from U_1 to U_2 or from U_2 to U_0 are also controlled. The first potential U_1 is selected to lie about 0.02 to 1 mV above the reference potential U_0, and the length of the first period of time T1 is about 100 milliseconds. The length of the second period of time T_2 is selected to amount to from about 0.2 to 1.5 times the first period of time T_1.

The second period of time T_2 can also be calculated from the measured sensor currents i_0, i_1 and i_2 on the basis of a simplified equivalent circuit diagram shown in Figure 3.

The measuring cell (1), Figure 1, can be

represented electrically by a measuring electrode capacitance C_m, which is made up of the measuring electrode (2) and the counterelectrode (3), with the electrolyte (6) situated between them, and a measuring electrode conductance G_m, which reflects the ohmic resistance between the electrodes (2, 3) and the contact resistances between the electrodes (2, 3) and the leads (8, 9).

The second period of time can be calculated from the formula

$$T2 = T_1 \times \ln(1 - Y \times (1/X))/\ln(X)$$

where

$$X = (i_1 - i_0)/(i_2 - i_0) \quad \text{and}$$

$$Y = (U_1 - U_0)/(U_2 - U_0).$$

The measuring electrode capacitance C_m and the measuring electrode conductance G_m are given by the calculation formulae:

$$G_m = (i_1 - i_0)/(U_1 - U_0)$$

$$C_m = T_1 \times G_m/\ln((i_1 - i_0)/(i_2 - i_0).$$

In the evaluation unit predetermined values for the measuring electrode capacitance and the measuring electrode conductance are stored as reference measuring electrode capacitance C_{m0} and as reference measuring electrode conductance G_{m0}, and in the evaluation unit a comparison of the calculated parameters C_m and G_m with the predetermined values C_{m0} and G_{m0} is performed.

Deviations of the parameters C_m, G_m from the preset values C_{m0}, G_{m0} can have the following causes:

For example, faulty contact with the measuring electrode only affects the measuring electrode conductance G_m, while reduced wetting of the measuring electrode (e.g. due to drying out) shows up predominantly in the measuring electrode capacitance C_m. Since in addition the temperature dependence of G_m and C_m cam readily be determined and moreover is approximately linear over a wide range, the possible

tolerance limits for C_m and G_m can be selected relatively narrowly. Consequently not only can a complete failure of the sensor be detected, but changes can already be recognised which would only lead to a failure later on, or which would have an unacceptable effect on the measuring properties of the sensor.

The method of the invention for the identification of faults can also be used in the same way for a three-electrode measuring cell (12) with a reference electrode, the equivalent circuit diagram of which is represented in Figure 4. Components in Figure 4 which are the same as in Figures 1 and 3 are indicated by the same reference numerals. The reference electrode, not shown in Figure 4, is connected to a lead (13). In the equivalent circuit diagram of Figure 4 G_g is the counterelectrode capacitance, C_g is the counterelectrode capacitance, G_r is the reference electrode conductance, and C_r is the reference electrode capacitance. The conductances can be physically understood as resistance of the leads to the electrodes, contact resistance between lead and electrode and contact resistance between electrode and electrolyte, and the capacitances are double layer capacitances between the electrodes.

CLAIMS

1. A method for identifying causes of faults in an amperometric measuring cell which has at least one measuring electrode and a counterelectrode in a soluble electrolyte-filled electrolyte chamber separated from the measuring sample being investigated by a permeable membrane, and which is connected to a voltage source which produces a sensor current between the electrodes and provides a potential, the method comprising the steps of:

applying a reference potential and measuring a reference current flowing due to the application of the reference potential;

applying a first potential, different from the reference potential, during a first period of time and measuring a first sensor current flowing due to the application of the first potential; and

comparing the first sensor current with the reference current.

2. A method for identifying causes of faults in an amperometric measuring cell as claimed in claim 1, wherein the first sensor current is measured shortly after the beginning and/or shortly before the end of the first period.

3. A method according to claim 1 or 2, in which during a second period of time following the first period of time the potential is adjusted to a second potential which is greater than the reference potential if the first potential is less than the reference potential and is less than the reference potential if the first potential is greater than the reference potential.

4. A method according to claim 3, wherein the length of the second period of time is not more than 1.5 times the first period of time.

5. A method according to claim 3, wherein the

second period of time is calculated by the formula:

$$T_2 = T_1 \times \ln(1 - Y \times (1/X))/\ln(X)$$

where

T_1 = first period of time

T_2 = second period of time

$X = (i_1 - i_0)/(i_2 - i_0)$

$Y = (U_1 - U_0)/(U_2 - U_0)$

i_0 = reference current

i_1 = sensor current shortly after start of first period

i_2 = sensor current shortly before end of first period

U_0 = reference potential

U_1 = first potential

U_2 = second potential.

6. A method according to one of claims 1 to 5, wherein the parameters C_m and G_m electrically representing the electrochemical measuring cell are calculated according to the formulae:

$$G_m = (i_1 - i_0)/(U_1 - U_0)$$

$$C_m = T_1 \times G_m/\ln((i_1 - i_0)/(i_2 - i_0).$$

T_1 = first period of time

i_0 = reference current

i_1 = sensor current shortly after start of first period

i_2 = sensor current shortly before end of first period

U_0 = reference potential

U_1 = first potential.

7. A method according to claim 6, characterised in that the parameters C_m and G_m are compared with preset values C_{m0} and G_{m0} in order to determine a fault in an amperometric measuring cell.

8. A method for identifying causes of faults in an amperometric measuring cell substantialy as herein described with reference to Figures 1-3 or 1, 2 and 4

of the accompanying drawings.

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The Patent Office

Application No:	GB 9526143.4	**Examiner:**	David Mobbs
Claims searched:	1-8	**Date of search:**	22 March 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): G1N NBKT.

Int Cl (Ed.6): G01N 27/416.

Other: NONE.

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
Y	WO 94/08235 A1 FOXBORO	1
Y	WO 90/12315 A1 NEOTRONICS	1

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
&	Member of the same patent family		